

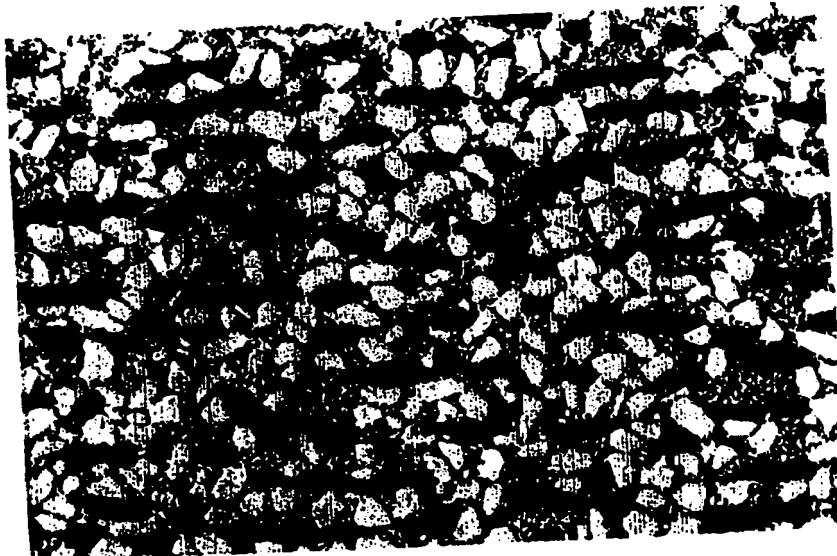


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(54) Title: NOVEL SILICON CARBIDE DUMMY WAFER		



100 μm

## (57) Abstract

The present invention relates to an unsiliconized or siliconized wafer consisting essentially of recrystallized silicon carbide, the wafer having a diameter of at least 150 mm and a thickness of between 0.5 and 2 mm, and having a porosity or free silicon content between 15 v/o and 43 v/o.

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## NOVEL SILICON CARBIDE DUMMY WAFER

## BACKGROUND OF THE INVENTION

The manufacture of semi-conductor devices such as diodes and transistors typically requires oxidizing the surfaces of thin silicon wafers, etching cavities in the surfaces of those wafers, and depositing a dopant (i.e., boron, phosphorous, arsenic, or antimony) in those cavities, thus forming transistor contact points. The oxidation and doping operations involve rapid heat and cool cycles in an electrically heated furnace at temperatures ranging from 1000°C to 1350°C. After the surface has been etched, the dopant is usually fed as a gas into the necked down end of a diffusion process tube placed in the furnace. The gas then diffuses into the etched cavities and deposits on its surfaces.

During the oxidation and diffusion steps, the silicon wafers sit on boats or plates placed within the process tube. The wafer boat and process tube are typically made of a material which has excellent thermal shock resistance, high mechanical strength, an ability to retain its shape through a large number of heating and cooling cycles, and which does not out-gas (i.e., introduce any undesirable impurities into the atmosphere of the kiln during firing operations). One material which meets these requirements is siliconized silicon carbide.

When the silicon wafers are processed in a boat, it is naturally desirable that each wafer in the boat be exposed to identical gas concentration and temperature profiles in order to produce consistent product. However, the typical hydrodynamic situation is such that consistent profiles are found only in the middle of the boat while inconsistent profiles are often found at the ends of the boats, resulting in undesirable degrees of dopant deposition upon the end-wafers which render them unusable.

One conventional method of mitigating this "end-effect" problem is to fill the end slots of the boat with sacrificial silicon wafers. However, it has been found that silicon wafers are expensive, extensively out-gas, warp at high process temperatures, flake particles, and have a short useful life span.

Another conventional method of mitigating the "end-effect" problem is to fill the end slots of the boat with "dummy" wafers. For example, one investigator placed SiC-coated carbon wafers having the exact dimensions of the neighboring silicon wafers in the end slots. However, these wafers were found to break apart, contaminating the furnace with the exposed carbon.

Another investigator proposed using CVD monolithic silicon carbide as a dummy wafer. However, this material is known to be very expensive.

Japanese Patent Publication 5-283306 discloses a siliconized silicon carbide dummy wafer having an alumina/silica coating.

Therefore, it is the object of the present invention to provide an inexpensive dummy wafer which possesses the dimensional, physical and mechanical properties required for dummy wafers.

#### SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided an unsiliconized wafer consisting essentially of recrystallized silicon carbide, the wafer having a diameter of at least 150 mm and a thickness of no more than 2 mm, and having a porosity of between 15 v/o and 43 v/o.

Also in accordance with the present invention, there is provided a recrystallized silicon carbide wafer having a diameter of at least 150 mm and a thickness of no more than 2 mm, and comprising between 15 v/o and 43 v/o free silicon, and a CVD silicon carbide coating thereon.

Also in accordance with the present invention, there is provided a recrystallized silicon carbide wafer having a diameter of at least 150 mm and a thickness of no more than 2 mm, and comprising between 25 and 40 v/o free silicon, the free silicon comprising coarse interconnected free silicon pockets having 5 to 50 micron diameters.

#### DESCRIPTION OF THE FIGURES

Figure 1 is a photomicrograph of conventional unsiliconized silicon carbide, wherein the light regions represent silicon carbide and the dark regions represent porosity.

Figure 2 is a photomicrograph of an unsiliconized embodiment of the present invention, wherein the light regions represent silicon carbide and the dark regions represent porosity.

5 DETAILED DESCRIPTION OF THE INVENTION

For the purposes of the present invention, "v/o" refers to a volume percent, "w/o" refers to a weight percent and a "conventionally produced" product refers to Si-SiC products made in accordance with US Patent No. 3,951,587 ("the Alliegro patent"). In addition, the term "flatness" is considered to be the maximum bow height from a mean datum line, the mean datum line being defined by an arbitrary diameter at the surface of the wafer.

10 The initial efforts of the present inventors examined siliconized silicon carbide, specifically CRYSTAR® (containing about 15% free silicon and about 85% bimodal SiC, manufactured by the Norton Company of Worcester, MA), as the dummy wafer material. However, it was found that the conventional CRYSTAR® casting process (a bimodal SiC blend slip-cast in a porous plaster mold) could not successfully produce a thick billet amenable to slicing. In particular, when the slip was slip-cast thicker than about 20 mm in depth, the resulting billet would develop cracks upon drying or firing due to residual stresses.

25 It is believed this process failed because water retained in the green body pores after slip-casting turned into entrapped steam upon subsequent heating. The internal pressure buildup generated by the steam forced the cast body to crack and warp. The present inventors noted the conventional slip cast approach produced only about 15 v/o porosity and pore channels of only about 2 microns (as measured by mercury porosimetry) in the cast body and hypothesized that this level of porosity was not substantial enough to provide continuous channels suitable for the escape of retained water during conventional drying. They also contemplated that the density gradients produced by conventional slip casting contributed to the cracking problem, as these gradients produced thermal stresses on heating.

The present inventors also examined open-face casting. The open face casting approach produced a thin wafer having a thickness of about 3 mm (to provide for warpage during firing) which was then surface ground to the desired 0.5 - 1.0 mm thickness. The fired product had a porosity of about 15-16 v/o. However, because the required grinding operation is labor intensive and removes over half of the wafer stock, open face casting was considered to be prohibitively inefficient and expensive. Further attempts to open face cast the slip closer to the desired wafer thickness resulted in green wafers that warped during drying and firing.

The present inventors then considered freeze-casting a bimodal silicon carbide slip and unexpectedly found that freeze casting provided a thick, dimensionally correct billet which did not warp or crack during processing, was easily sliced, and maintained sufficient strength after it was sliced.

It is believed that the freeze casting process yields a green body billet which is particularly suited to the requirements of large scale production of SiC dummy wafers. When a slip is freeze cast, the water undergoes a 4% volume expansion as it becomes ice crystals. Since freeze casting is performed in a closed volume, the ice particle expansion has the effect of packing the SiC particles closer together (when compared to slip cast SiC packing) in the regions not taken up by the ice particles. Moreover, it has been observed that the ice crystals formed in freeze casting are interconnected, thereby forming pore channels upon drying. Therefore, although the freeze cast body possesses the same overall volume percent solids as the conventional slip cast body (i.e., about 72 v/o), the freeze cast body has both larger, interconnected pores and better interparticle bonding. The better interparticle bonding provides not only good strength for the cast body (despite the larger pore size) but also good strength for the sintered body, as the more highly packed SiC grains more readily form necks during recrystallization. Because the interconnected pores provide a channel for steam escape and the superior particle bonding provides superior strength, it appears that freeze casting avoids the problems encountered in the conventional

slip casting process for large scale SiC dummy wafer production.

Another advantage of the present invention is that its preferred process need not include the vacuum sublimation step typically required during conventional silicon carbide freeze casting. Without wishing to be tied to a theory, it is believed that vacuum sublimation is not required because compaction of the SiC grains during freezing yields a relatively rigid skeletal structure resistant to movement (and therefore cracking) when the water is removed. In addition, the relatively large pore channels formed by the ice crystals provide reduced capillary pressures and reduced drying stresses.

In one preferred embodiment of the present invention, a SiC-based wafer is made and used in a process comprising:

- a) mixing silicon carbide powder, water, and an ice-crystal growth inhibitor to produce a slip,
- b) freezing the slip at about -85°C to produce a frozen casting,
- c) air drying the frozen casting to partially remove the water,
- d) drying the casting at about 200°C for about 24 hours,
- e) vacuum presintering the body to produce a recrystallized billet having a green strength of about 35 MPa,
- f) slicing the billet into wafers,
- g) optionally, siliconizing and/or CVD coating the wafers, and
- h) placing the wafers in a boat.

In the above-described embodiment, the slip typically comprises a bimodal SiC powder distribution comprising between about 15 and about 41 v/o coarse SiC grains having a particle size ranging from 10 to 150 microns ("the coarse fraction"), and between about 34 and about 60 v/o fine SiC grains having a particle size ranging between 1 and 4 microns ("the fine fraction"). Preferably, the fine fraction comprises between about 36 and 42 v/o of the slip and has an average particle size of about 2-3 microns, while the coarse fraction comprises

between 33 v/o and 38 v/o of the slip and has an average particle size of about 60 microns. When the coarse SiC particle size is above about 150 microns, it approaches half the cross-section of the final wafer and grain pullout during slicing is observed in the finished wafer.

Water is generally included in the slip in an amount sufficient to produce a slip having from about 50 to 85 v/o solids. However, other solvents amenable to freeze casting (such as glycerol, ethanol, methanol, hexane) may be suitably used as the slip's liquid carrier.

The slip also preferably contains an ice-crystal growth inhibitor. Typical freeze casting techniques create ice crystals as large as 5000-10000 um on both the inside and outside of the frozen casting. Subsequent freeze drying and firing of these bodies reveal large isolated pores (the remnants of the large ice crystals). These isolated pores act as flaws which degrade both green and final strength. The ice-crystal growth inhibitor prevents large crystal formation by forcing the slip to freeze in the form of minute crystals on the order of only 5-50 microns. Typical ice crystal growth inhibitors include hydrogen bond-forming compounds such as glycerol and all of the compounds similarly identified in U.S. Patent No. 4,341,725 ("the Weaver patent"), the entire specification of which is incorporated by reference.

Typically, the ice crystal growth inhibitor comprises between about 0.2 w/o and about 5 w/o of the slip, preferably between about 1 w/o and about 1.5 w/o. In more preferred embodiments, glycerol comprises about 1 w/o of the slip. The required amount of ice crystal growth inhibitor also depends on the solids content of the slurry, with high solids content slurries requiring less inhibitor. Other typical components of the slip include conventional amounts of conventional casting additives.

For example, deflocculating agents such as NaOH and  $\text{Na}_2\text{SiO}_3$  may be used. A binder may also be present in the range from about 0.25 w/o to 4.0 w/o solids. In preferred embodiments, an acrylic latex binder is used at a level of about 1 w/o of the solids.

In order to insure a homogeneous slip, the slip components are typically mixed in a ball mill evacuated to a



vacuum level of between about 27 and 30 inches Hg and rolled for at least about 17 hours.

The freezing step of this embodiment (often called, "freeze casting") preferably includes pouring the slip into an impermeable mold and lowering its temperature until the liquid carrier freezes, thereby solidifying the slip. Freezing the slip generally entails lowering its temperature to between about  $-20^{\circ}\text{C}$  and  $-100^{\circ}\text{C}$  for between about 30-180 minutes, resulting in a freeze-cast body having only small (i.e., 5-50 micron) ice crystals. Preferably, the impermeable mold is made of silicone rubber which can be easily peeled from the frozen body.

The air drying step of the preferred embodiment serves to remove enough free water from the casting to allow it to be placed in a heated oven without cracking. Air drying can be effectuated by simply removing the frozen body from its mold and letting it stand in air for about 24 hours. Typical conditions and drying times for air drying range between 20 and  $30^{\circ}\text{C}$ , preferably  $25^{\circ}\text{C}$ ; between about 0.01 and several atm pressure, preferably 1 atm pressure; and between about 18 and about 48 hours, preferably about 24 hours.

The high temperature drying step of the above embodiment is typically performed at a higher temperature and for a longer duration than the air drying step and removes essentially all the absorbed water in the casting. Typical conditions and drying times for this step range from between  $80^{\circ}\text{C}$  and  $200^{\circ}\text{C}$ , preferably  $140^{\circ}\text{C}$ ; between about 0.01 and 1 atm pressure, preferably 1 atm pressure; and between about 18 and about 48 hours, preferably about 24 hours. It was unexpectedly found that the freeze cast body can be suitably dried at atmospheric pressure under these conditions without cracking. As noted above, conventionally processed, slip cast SiC bodies were found to crack under high temperature, atmospheric drying conditions. Because the freeze drying process does not require subsequent vacuum drying, it is significantly less expensive than conventional SiC processing.

The dried casting produced in accordance with this embodiment exhibits a bulk density of at least about 1.8 g/cc and a four point bending strength of at least about 5 MPa. Its

pore size ranges from about 5 to 50 microns. Its average pore size is about 15 microns. In contrast, the conventional dried SiC casting has an average pore size of only about 2 microns.

The vacuum presintering step of the preferred embodiment serves to establish recrystallization (i.e., neck growth  
5 between the SiC grains without densification) without cracking.

It may be carried out at about 1900-1950°C under a vacuum of about 0.5 torr in an Ar atmosphere. Whereas conventional SiC castings were found to crack under these conditions, it is  
10 believed the freeze cast bodies of the present invention did not crack because the relatively large pore channels formed by the ice crystals result in low capillary pressures and low stresses on drying, as well as a uniform density across the part which resists thermal stresses.

15 The recrystallized billet produced in accordance with this embodiment exhibits a bulk density of at least about 1.8 g/cc.

Its porosity ranges from 25 v/o to 43 v/o. Its pore size ranges from about 5 to 50 microns. Its average pore size is about 15 microns. In contrast, the conventional recrystallized  
20 SiC casting has a porosity of about 16 v/o and an average pore size of about 2 microns. Its strength (as measured by ring on ring biaxial flexure) is at least 30 MPa, typically between 30 and 50 MPa.

After presintering, the recrystallized billet is sliced by  
25 conventional processes (i.e., a diamond wheel or wire) to its final dimension. In contrast to less porous conventional SiC billets, the recrystallized SiC billet of this embodiment is easily sliced into thin SiC wafers. The structure of the presintered billet is such that it has sufficient handling  
30 strength, but is quickly and easily sliced to a good surface finish and flatness. For example, a 1 mm thick wafer produced in accordance with the present invention may be sliced from a 15 cm diameter billet in only about 5 minutes. In contrast, it is believed that a higher density slip cast SiC billet would  
35 require about 60 minutes and a fully dense SiC billet would require about 120 minutes to slice. Recrystallized silicon carbide dummy wafers having diameters of between about 150 and about 300 mm, thicknesses between about 0.5 and about 2 mm, preferably between 0.5 mm and 1.5 mm, more preferably between

about 0.5 and 1.0 mm; and flatnesses of between about 25 and about 100 microns, preferably less than about 50 microns, are obtainable in accordance with this embodiment, usually after mere diamond saw slicing. If the wafer is subsequently  
5 siliconized, it may need to be rotary ground for a short period to remove a few microns and attain a flatness of less than 100 um.

The final firing step makes the wafer impermeable to gases or liquids. It typically involves either impregnating the  
10 porous wafer with silicon to eliminate porosity and/or CVD coating it with an impermeable ceramic such as silicon carbide.

If siliconizing is selected, it may be carried out in accordance with US Patent No. 3,951,587 ("the Alliegro patent"), the specification of which is incorporated by  
15 reference. It was unexpectedly observed that the siliconized wafers had a flatness of about 100 um. In contrast, dimensionally similar conventional "green" SiC castings have been found to excessively warp, necessitating a thicker casting and expensive final machining in order to produce the same flat  
20 product.

The siliconized wafer of a preferred embodiment of the present invention exhibits a bulk density of at least about 2.75 g/cc. Its pockets of free silicon range from about 5 to 50 microns in diameter. It is fully dense. In contrast, a  
25 conventionally produced siliconized SiC wafer has pockets of free silicon that are only about 2 microns in diameter.

The microstructure of this embodiment of the present invention appears to have three distinct phases of the material, comprising: a coarse grain SiC phase, a coarse free  
30 silicon phase; and a mixed phase comprising fine SiC grains and fine free silicon pockets. Depending upon whether the SiC dummy wafer is siliconized, the SiC wafer typically comprises:

- a) between about 15 v/o and 41 v/o (preferably 33 to 38 v/o) silicon carbide grains having a diameter of between  
35 10 um and 150 um,
- b) between about 34 v/o and 60 v/o (preferably 36 to 42 v/o) silicon carbide grains having a diameter of between 1 um and 4 um, and
- c) between 25 v/o and 40 v/o free silicon or porosity.

The porosity of the unsiliconized wafer is characterized by a bimodal size distribution of coarse (5-50  $\mu\text{m}$ ) pores and fine pores, while the free silicon of the siliconized wafer is characterized by free silicon pockets having 5-50 micron diameters and a free silicon matrix which surrounds fine SiC grains. See Figure 2. In some embodiments, there is preferably between 35 v/o and 40 v/o free silicon. In comparison, prior art microstructures were found to be characterized by a uniform structure of a mixed phase comprising large grain SiC, small grain SiC and small free silicon pockets or porosity. See Figure 1.

Sandblasting of the siliconized SiC wafer can remove excess free silicon that has exuded to the surface due to the volume expansion of silicon on solidification, and may be done by conventional sandblasting processes. Because these wafers possess high strength, they do not break when subjected to sandblasting.

Although the above-described embodiment of the present invention exploits freeze casting to produce a thin, strong SiC wafer, it is also anticipated that useful SiC wafers can be obtained by a number of alternative processes, including: a) warm pressing a SiC billet at 1750°C and 3000 psi; b) gel casting and presintering a SiC billet in accordance with U.S. Patent No. 5,145,908; c) cold isostatic pressing a SiC billet, and d) tape casting or roll pressing and then recrystallizing a SiC slip to produce a fired SiC wafer having a porosity of about 21%.

The novel recrystallized silicon carbide ceramics of the present invention may be used in conventional siliconized silicon carbide or CVD coated silicon carbide applications, including those applications disclosed in the Alliegro patent.

It may also find application as a rigid disc in computer hard drives, as a substrate for other electronic applications, or as baffle plates in wafer boats. In particular, there is contemplated a silicon carbide disk substrate for use in a disk drive assembly having a head and a disk, the disk comprising the disk substrate, wherein the disk substrate comprises a) between 15 v/o and 43 v/o free silicon or porosity, preferably between 25 v/o and 40 v/o; b) preferably having a flatness of

between 25 um and 100 um; c) preferably having a bimodal SiC grain distribution of coarse and fine grains; and d) preferably having a bimodal free silicon or pore distribution of coarse and fine pores. Other contemplated uses of the highly porous silicon carbide discs of the present invention (which could exploit the low pressure drop across the disc) include gas burner plates, composite substrates and filters.

In some embodiments, the porous wafer of the present invention is optionally coated with a layer of either polysilicon, silicon nitride or silicon dioxide, placed in a diffusion boat in which silicon wafers are also subsequently, and the silicon wafers are processed at a temperature of at least about 600 degrees C.

In some embodiments, the siliconized, SiC CVD coated wafer of the present invention is placed in a diffusion boat in which silicon wafers are subsequently placed, and the wafers are processed at temperatures above 1000 degrees C. It is believed the CVD SiC coating is necessary at those temperatures to prevent oxidation of the SiC grains. Therefore, there is also provided a process comprising:

- a) placing a silicon wafer in a diffusion boat having the siliconized, SiC CVD coated wafer of the present invention placed therein, and
- b) processing the silicon wafer at a temperature above about 1000 degrees C.

Also in accordance with the present invention, there is provided a method of single wafer processing, comprising the steps of:

- a) providing a silicon carbide wafer of the present invention (preferably having a diameter of at least 200 mm and more preferably at least 300 mm) in a substantially horizontal position, and
- b) placing a silicon wafer (preferably having a diameter of at least 200 mm and more preferably at least 300 mm) upon the silicon carbide disc, and
- c) heating the silicon wafer at a rate of at least 100 C per second.

Also in accordance with the present invention, there is provided a method of cleaning single wafer processing chambers,

comprising the steps of:

- a) providing a susceptor in a processing chamber,
- b) placing a silicon wafer upon the susceptor,
- c) processing the silicon wafer,
- 5 d) removing the silicon wafer,
- e) placing a silicon carbide wafer of the present invention (preferably having a diameter of at least 200 mm and more preferably at least 300 mm) over the susceptor, and
- f) cleaning the processing chamber.

10 Also in accordance with the present invention, there is provided a method of flat panel display processing, comprising the steps of:

- a) providing a silicon carbide wafers method of the present invention (preferably having a length of at least 165 mm and
- 15 a width of at least 265 mm) in a substantially horizontal position, and
- b) placing a flat glass plate (preferably having and length and width of at least 100 mm) upon the silicon carbide disc, and
- 20 c) processing the flat glass plate.

Also in accordance with the present invention, there is provided a method of plasma etching silicon wafers, comprising the steps of:

- a) providing a silicon wafer having a predetermined diameter
- 25 of at least 200 mm,
- b) placing a silicon carbide ring of the present invention (having an inner diameter essentially equal to the predetermined diameter of the silicon wafer) around the silicon wafer, and
- 30 b) plasma etching (preferably dry metal plasma etching) the silicon wafer.

#### EXAMPLE I

A freeze cast slurry was prepared by mixing the following materials in the quantities shown in Table I, and rolling in a

35 jar for 18 hours.

TABLE I

Silicon Carbide (3 micron)	4680g
Silicon Carbide (100F)	4320g
Water	1080g

BASF Acranol 290D Binder	137g
NaOH (1N)	81g
Baker Glycerol	90g

The slurry was vacuum deaired and poured into a polyvinyl chloride tube having an inner diameter of 6", an outer diameter of 6.5" and a height of 10". The tube was clamped to a glass plate to prevent leakage and form the bottom surface. The assembly was then placed in a freezer at -85°C for 3 hours. After being fully frozen, the tube was cut away from the billet. The freeze cast billet was initially air dried at about 25°C for 18 hours and final dried at 140°C for 48 hours to remove the absorbed water. The billet was then sintered at about 1900°C in an argon atmosphere to effect recrystallization. The porous recrystallized billet was dry sliced with a metal bonded diamond saw to a thickness of 0.040". The wafer was infiltrated with molten silicon at about 1800°C in an argon/nitrogen atmosphere and then sandblasted with SiC grain to remove any excess silicon. The sandblasted wafer had a flatness of about 100 microns. Rotary grinding with a diamond abrasive provided a flatness of about 50 microns. It is contemplated that final lapping with a boron carbide slurry could produce flatness of 20 microns.

#### EXAMPLE II

A unimodal silicon carbide slip having an average size of 3 microns was hot pressed in a graphite die at about 1850°C and 3000 psi for 1 hour. The billet had a 3" diameter, a 4" height, and a density of about 2.0 g/cc (about 62% of theoretical density). The billet was dry sliced with a metal bonded diamond wheel to a thickness of 0.75 mm. The wafer was infiltrated with molten silicon at about 1800°C in an argon/nitrogen atmosphere. The siliconized wafer was then sandblasted with SiC grain to remove any excess silicon. The siliconized wafer had a flatness of about 70 microns. Some of the sandblasted wafers were coated with about 50 microns of SiC by chemical vapor deposition of methyltrichlorosilane in hydrogen and argon at about 1100°C.

We claim:

1. An unsiliconized wafer consisting essentially of recrystallized silicon carbide, the wafer having a diameter of at least 150 mm and a thickness of between 0.5 and 2 mm, and having a porosity of between 15 v/o and 43 v/o.
2. The wafer of claim 1 wherein the wafer has a thickness of between 0.5 mm and 1.5 mm.
3. The wafer of claim 2 wherein the wafer has a diameter of no more than 300 mm.
4. The wafer of claim 3 having a porosity of between 25 v/o and 40 v/o.
5. The wafer of claim 3 wherein the silicon carbide consists of silicon carbide grains.
6. The wafer of claim 4 wherein the porosity is characterized by coarse interconnected pores having a diameter of between 5 and 50 microns um.
7. The wafer of claim 6 having a thickness of between 0.5 and 1 mm.
8. The wafer of claim 6 wherein the coarse pores have a diameter of about 15 microns.
9. The wafer of claim 4 wherein the SiC has a bimodal size distribution comprising coarse grains and fine grains.
10. The wafer of claim 9 wherein the coarse grains have a diameter of between 10 and 150 microns.
11. The wafer of claim 10 wherein the fine grains have a diameter of between 1 and 4 microns.
12. The wafer of claim 12 wherein the coarse grains comprise between 15 and 41 v/o of the wafer.
13. The wafer of claim 12 wherein the fine grains comprise between 34 and 60 v/o of the wafer.
14. A recrystallized silicon carbide wafer having a diameter of at least 150 mm and a thickness of no more than 2 mm, and comprising between 15 v/o and 43 v/o free silicon, and a CVD silicon carbide coating thereon.
15. The wafer of claim 14 wherein the wafer has a thickness of between 0.5 mm and 1.5 mm.
16. The wafer of claim 15 wherein the wafer has a diameter of no more than 300 mm.



17. The wafer of claim 16 comprising between 25 v/o and 40 v/o free silicon.
18. The wafer of claim 17 having a flatness of between 25 um and 100 um.
- 5 19. The wafer of claim 17 wherein the free silicon comprises coarse interconnected free silicon pockets having 5 to 50 micron diameters.
20. The wafer of claim 19 having a thickness of between 0.5 and 1 mm.
- 10 21. The wafer of claim 17 wherein the SiC has a bimodal size distribution comprising coarse SiC grains and fine SiC grains.
22. The wafer of claim 21 wherein the coarse SiC grains have a diameter of between 10 and 150 microns.
- 15 23. The wafer of claim 22 wherein the fine SiC grains have a diameter of between 1 and 4 microns.
24. The wafer of claim 21 wherein the coarse SiC grains comprise between 15 and 41 v/o of the wafer.
25. The wafer of claim 21 wherein the fine SiC grains comprise between 34 and 60 v/o of the wafer.
- 20 26. A process comprising:
  - a) forming a slip comprising silicon carbide,
  - b) freezing the slip to produce a frozen casting,
  - c) drying the casting,
  - 25 d) recrystallizing the casting to produce a billet, and
  - e) slicing the billet to produce a plurality of silicon carbide wafers of claim 1.
27. The process of claim 26 further comprising the step of:
  - f) siliconizing the wafer.
- 30 28. The process of claim 26 further comprising the step of:
  - f) coating the wafer with CVD silicon carbide.
29. The process of claim 26 wherein the slip comprises silicon carbide powder, water, and an ice-crystal growth inhibitor.
- 35 30. The process of claim 26 wherein the drying step consists essentially of i) air drying the frozen casting to partially remove the water and ii) drying the casting at about 200°C for about 24 hours.

31. A method of using a silicon carbide wafer comprising the steps of:
- a) placing a silicon wafer in a diffusion boat in which the wafer of claim 14 is also placed.
- 5 32. The process of claim 31 further comprising:
- b) processing the silicon wafer at a temperature above about 1000 degrees C.
- 10 33. A recrystallized silicon carbide wafer having a diameter of at least 150 mm and a thickness of no more than 2 mm, and comprising between 25 and 40 v/o free silicon, the free silicon comprising coarse interconnected free silicon pockets having 5 to 50 micron diameters.
- 15 34. The wafer of claim 33 having a diameter of between 150 and 300 mm.
35. The wafer of claim 34 having a thickness of between 0.5 and 1.5 mm.
- 20 36. The wafer of claim 35 having a thickness of between 0.5 and 1 mm.
37. A method of using a silicon carbide wafer comprising the steps of:
- a) placing a silicon wafer in a diffusion boat in which the wafer of claim 1 having a coating selected from the group consisting of polysilicon, silicon dioxide and silicon nitride is also placed therein.
- 25 38. The method of claim 37 further comprising:
- b) processing the silicon wafer at a temperature above about 600 degrees C.
- 30 39. A method of using a silicon carbide wafer comprising the steps of:
- a) placing a silicon wafer in a diffusion boat in which the wafer of claim 33 is also placed.
- 35 40. The method of claim 39 further comprising:
- b) processing the silicon wafer at a temperature above about 1000 degrees C.

## AMENDED CLAIMS

[received by the International Bureau on 30 July 1996 (30.07.96);  
original claims 1-4, 7, 14-19 and 21 amended;  
remaining claims unchanged (3 pages)].

## We claim:

1. An unsiliconized wafer consisting essentially of recrystallized silicon carbide, the wafer having a diameter of at least 150 mm and a thickness of between 0.5 and 1 mm, and having a porosity of between 15 v/o and 43 v/o.
2. The wafer of claim 1 having a porosity characterized by an average pore size of 2 um.
3. The wafer of claim 1 wherein the wafer has a diameter of no more than 300 mm.
4. The wafer of claim 1 having a porosity of between 25 v/o and 40 v/o.
5. The wafer of claim 3 wherein the silicon carbide consists of silicon carbide grains.
6. The wafer of claim 4 wherein the porosity is characterized by coarse interconnected pores having a diameter of between 5 and 50 microns um.
7. The wafer of claim 1 having a flatness of between 25 um and 100 um.
8. The wafer of claim 6 wherein the coarse pores have a diameter of about 15 microns.
9. The wafer of claim 4 wherein the SiC has a bimodal size distribution comprising coarse grains and fine grains.
10. The wafer of claim 9 wherein the coarse grains have a diameter of between 10 and 150 microns.
11. The wafer of claim 10 wherein the fine grains have a diameter of between 1 and 4 microns.
12. The wafer of claim 12 wherein the coarse grains comprise between 15 and 41 v/o of the wafer.
13. The wafer of claim 12 wherein the fine grains comprise between 34 and 60 v/o of the wafer.
14. The wafer of claim 1 having a porosity of between 15 v/o and 16 v/o.
15. The wafer of claim 14 having a porosity characterized by an average pore size of about 2 microns.
16. The wafer of claim 1 wherein the silicon carbide is recrystallized at between 1900 C and 1950 C.
17. The wafer of claim 40 comprising between 15 v/o and 41 v/o silicon carbide grains having a diameter of between 10 um

and 150  $\mu\text{m}$ , and between 34 v/o and 60 v/o silicon carbide grains having a diameter of between 1  $\mu\text{m}$  and 4  $\mu\text{m}$ .

18. A recrystallized silicon carbide wafer having a diameter of at least 150 mm and a thickness of no more than 2 mm, and comprising between 15 v/o and 43 v/o free silicon, a CVD silicon carbide coating thereon, and a flatness of between 25  $\mu\text{m}$  and 100  $\mu\text{m}$ .

19. The wafer of claim 18 wherein the free silicon comprises coarse interconnected free silicon pockets having 5 to 50 micron diameters.

20. The wafer of claim 19 having a thickness of between 0.5 and 1 mm.

21. The wafer of claim 18 wherein the SiC has a bimodal size distribution comprising coarse SiC grains and fine SiC grains.

22. The wafer of claim 21 wherein the coarse SiC grains have a diameter of between 10 and 150 microns.

23. The wafer of claim 22 wherein the fine SiC grains have a diameter of between 1 and 4 microns.

24. The wafer of claim 21 wherein the coarse SiC grains comprise between 15 and 41 v/o of the wafer.

25. The wafer of claim 21 wherein the fine SiC grains comprise between 34 and 60 v/o of the wafer.

26. A process comprising:

- a) forming a slip comprising silicon carbide,
- b) freezing the slip to produce a frozen casting,
- c) drying the casting,

- d) recrystallizing the casting to produce a billet, and
- e) slicing the billet to produce a plurality of silicon carbide wafers of claim 1.

27. The process of claim 26 further comprising the step of:  
f) siliconizing the wafer.

28. The process of claim 26 further comprising the step of:  
f) coating the wafer with CVD silicon carbide.

29. The process of claim 26 wherein the slip comprises silicon carbide powder, water, and an ice-crystal growth inhibitor.

30. The process of claim 26 wherein the drying step consists essentially of i) air drying the frozen

casting to partially remove the water and ii) drying the casting at about 200°C for about 24 hours.

31. A method of using a silicon carbide wafer comprising the steps of:

a) placing a silicon wafer in a diffusion boat in which the wafer of claim 14 is also placed.

32. The process of claim 31 further comprising:

b) processing the silicon wafer at a temperature above about 1000 degrees C.

33. A recrystallized silicon carbide wafer having a diameter of at least 150 mm and a thickness of no more than 2 mm, and comprising between 25 and 40 v/o free silicon, the free silicon comprising coarse interconnected free silicon pockets having 5 to 50 micron diameters.

34. The wafer of claim 33 having a diameter of between 150 and 300 mm.

35. The wafer of claim 34 having a thickness of between 0.5 and 1.5 mm.

36. The wafer of claim 35 having a thickness of between 0.5 and 1 mm.

37. A method of using a silicon carbide wafer comprising the steps of:

a) placing a silicon wafer in a diffusion boat in which the wafer of claim 1 having a coating selected from the group consisting of polysilicon, silicon dioxide and silicon nitride is also placed therein.

38. The method of claim 37 further comprising:

b) processing the silicon wafer at a temperature above about 600 degrees C.

39. A method of using a silicon carbide wafer comprising the steps of:

a) placing a silicon wafer in a diffusion boat in which the wafer of claim 33 is also placed.

40. The method of claim 39 further comprising:

b) processing the silicon wafer at a temperature above about 1000 degrees C.

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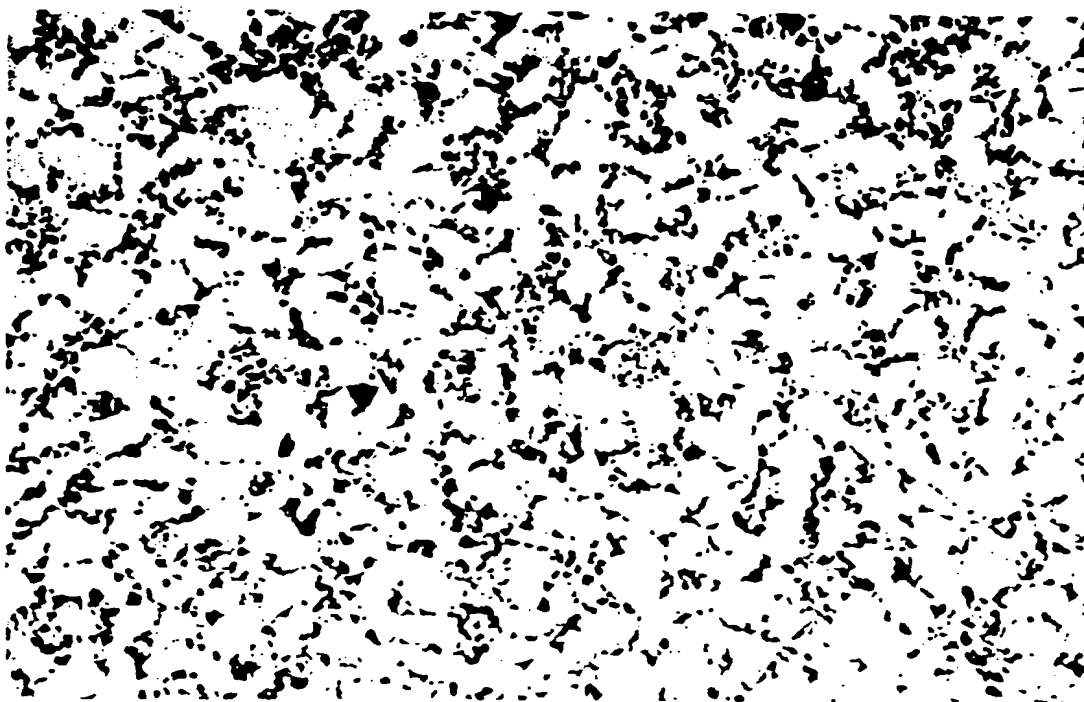


FIG. 1 PRIOR ART

100  $\mu\text{m}$

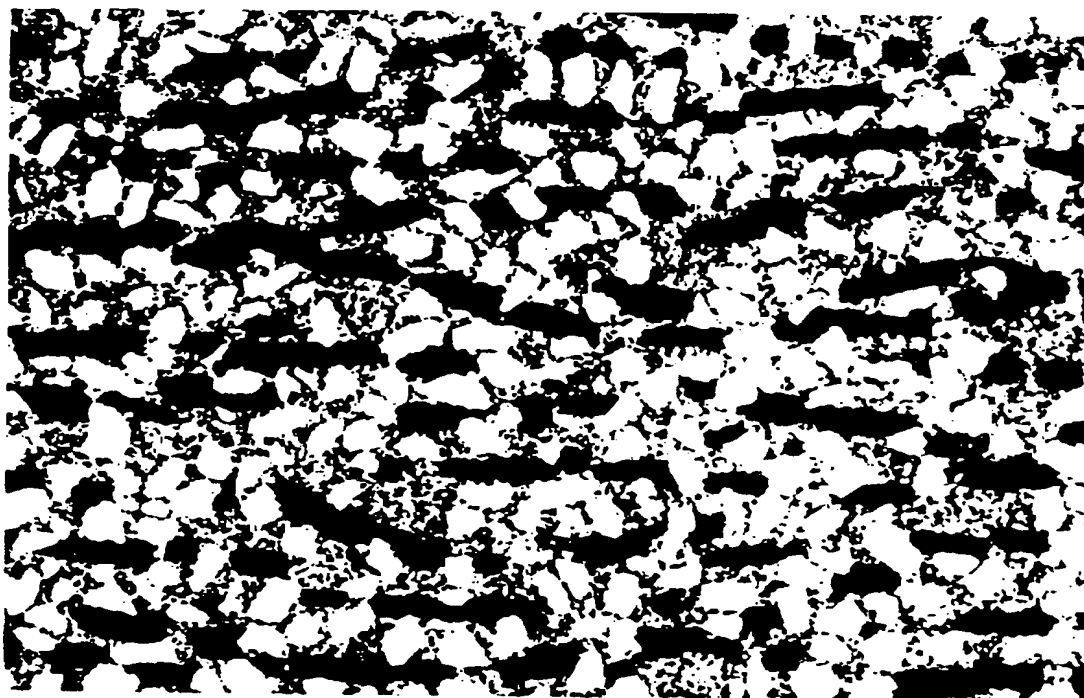


FIG. 2

100  $\mu\text{m}$

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/02880

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C04B35/573 C30B31/10 C04B41/87 C04B38/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C04B C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 486 938 (ASAHI GLASS COMPANY LTD.) 27 May 1992	1-5
Y	see page 5, line 20 - line 43; claims 1,7,8; examples 1,3,6,8,9	9-17, 21-25, 31,37
Y	EP,A,0 147 478 (HOECHST CERAMTEC AG) 10 July 1985 see claims 1,2; example 1	9-13, 21-25
Y	EP,A,0 340 802 (SHIN-ETSU CHEMICAL COMPANY, LTD.) 8 November 1989 see claims 1,3	14-17, 21-25, 28,31
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☒ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

14 June 1996

Date of mailing of the international search report

- 1. 07. 96

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 96/02880

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 341 725 (G.Q. WEAVER ET AL.) 27 July 1982 cited in the application	26,27, 29,30
Y	see claim 1; examples 1,2 ---	28
Y	PATENT ABSTRACTS OF JAPAN vol. 18, no. 63 (E-1500), 2 February 1994 & JP,A,05 283306 (TOSHIBA CERAMICS CO. LTD.), 29 October 1993, cited in the application see abstract -----	37



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/02880

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-486938	27-05-92	JP-A- 5032458 JP-B- 7084351 US-A- 5179049	09-02-93 13-09-95 12-01-93
EP-A-147478	10-07-85	NONE	
EP-A-340802	08-11-89	JP-A- 1282152 JP-A- 1282153 DE-D- 68909481 DE-T- 68909481 US-A- 4999228	14-11-89 14-11-89 04-11-93 28-04-94 12-03-91
US-A-4341725	27-07-82	NONE	

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